

ACCEPTABILITY OF ALCOHOLS AS GASOLINE SUBSTITUTES

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Automobile engines and their fuel systems were developed to use gasoline and their design has been progressively improved for that specific mixture of hydrocarbon fuels. Minor variations in design may render one engine more suitable for "regular" grade (92 RON) fuel while another may be able to use 98 octane fuel to a higher efficiency, but most vehicle owners wish to take advantage of their own preference at the filling station so that one versatile design of engine is required.

The introduction of alcohols (or other oxygenates) presents a range of new properties which may affect engine performance in various ways. Significant differences in volatility, calorific value and latent heat of vapourisation indicate the need for some major adjustments in engine and fuel system dimensions and design for engines which are to use 100% alcohol fuels.

However, there is much to gain by the use of gasohol mixtures since redesign of the internal combustion engine can then proceed by incremental changes rather than a "step change" of unacceptable magnitude. In a large population it is not easy to introduce new fuels unless and in so far as they can be used with minor adjustments only. e.g. to carburettor needle valves or idling controls, etc.

The research described in this paper studied the extent to which alcohols may be substituted without major alterations and especially their acceptability with regard to possible corrosive or deleterious effects on engine and fuel system materials.

Oxidation and corrosion test procedures

Test procedures were designed to simulate actual conditions during engine operation. Small samples of metal or carburettor parts etc., were totally immersed in the test fuel for periods of up to many weeks. While many tests were carried out at ambient temperatures, some higher temperature tests (50°C, 65°C, 90°C) were studied. In all cases periodic aeration of the test fuel reservoir (15 minutes each four hour period) was instigated in order to simulate actual conditions which would obtain in engine operation. Prior to the tests, specimens were ultrasonically cleaned in acetone and similarly cleaned before subsequent weighing and examination.

Corrosion and Oxidation

Corrosion of metals will usually proceed through the formation of an oxide layer on the accessible surface. If this layer is discontinuous as for example in the rusting of iron then corrosion proceeds steadily "eating" into the original material depth. However, if a continuous oxide film results as with some non-ferrous metals then, as oxidation progresses, flakes of oxide layers will detach themselves from the metal surface leaving new accessible surface. In general oxidation follows three courses. Most equations which explain the transient growth at lower temperatures involve logarithmic or exponential terms. They are grouped together as the log laws. At higher temperatures the oxide thickening obeys a parabolic law. This pattern involves a greater risk of flaking or cracking (Fig. 1).

Depending on the temperature and time a metal-oxygen system may follow any one of the above curves. A material which thickens by the parabolic law is accepted as reasonably resistant. However, there is a higher risk of cracking and flaking. If, in contrast the oxidation process follows the log laws then oxidation will almost reach a stand still at a small oxidation thickness. Component designers must therefore seek a material which thickens according to a favourable growth law. Alloying materials can often be found which though not altering the growth law will vary the rate of growth. In some cases the alloying constituent may introduce a new phase at the base of the oxide layer and then the effect of the alloy may give rise to a log law. To some extent the oxidation pattern may then be more predictable. At lower temperatures, as in this work, mechanical separation of the oxide layer may be greatly delayed, at least for a considerable time until a critical thickness is reached. The growth pattern may be altered so that a parabolic thickening at one temperature range may be replaced by rectilinear growth at higher temperatures. Material selection is thus founded on a range of complex ambient influences.

In the case of carburettor components, temperature variation is naturally restricted to liquid phase fuel temperatures and thus growth law prediction is simplified.

Corrosion in engine fuel systems

Corrosion and oxidation rates will be governed by several variables which in engine fuel systems will be dependent on ambient conditions, driving modes, and several design features. Oxidant concentration (in blends) will usually increase corrosion rate. Increased temperatures will also normally increase corrosion rates except where the increased temperature reduces oxygen content of the blend. Acidity (pH value) of the liquid corrodant is a crucial factor determining the likelihood and/or extent of corrosion. Since the oxidation products of alcohols and other oxygenates are carboxylic or other acids, the "strength" of the acid resulting from oxidation is of prime importance. Aeration, resulting in greater access to oxygen, will normally accelerate corrosion/oxidation effects unless the metal or material surface is passive. Flow velocity effects may be significant if corrosion reactions are "diffusion-controlled". Increased velocity will ensure a plentiful supply of fresh ions and will remove corrosion/oxidation products which otherwise would be potentially inhibiting.

In the case of vehicle engines, corrosion/oxidation rates may be of less direct significance than flaking or spalling and consequent weight loss effects. Thus, in this work we placed greater emphasis on any weight loss or gain resulting from corrosion. Samples were treated in significantly lengthy experiments being periodically removed from the test fuel reservoir for weighing. In this way a progressive weight gain and loss profile gave a more or less quantitative indication of corrosion and spalling effects. Figures 2 and 3 are typical of such measurements.

As a further indicator of potential corrosive attack, electrical conductivity of the substitute fuels and of gasohol blends was measured. Methanol (and its blends with gasoline) was shown to be more electrically conductive than ethanol. Some correlation with greater corrosion by methanol was found but other factors contributed significantly, masking this effect.

Vulnerability of metals to alcohols

A longer term study of a greater range of metals and alloys would be needed to identify the most resistant material for use with alcohols in fuel systems. However this work provided some clear indication of which metals might be the most vulnerable in the longer term.

The brasses for example showed greater surface damage in methanol than ethanol but their general resistance to spalling or weight loss indicated that brass components would be satisfactory at elevated temperatures and with aeration. Higher temperature accelerates acid formation in the alcohols giving rise to more severe attack on some metal surfaces. Copper surfaces for instance are highly vulnerable to pitting when in contact with formic acid in methanol. Aluminium is also severely attacked by methanol although the presence of formic acid shows little added effect.

Stainless steel components in methanol (with or without acid) are largely unaffected but this material would be too costly for many components and does not lend itself to simple fabrication techniques as do the "softer" non-ferrous metals copper, zinc, aluminium and their alloys.

Zinc carburettor components showed greater surface damage in methanol than ethanol as judged by the dulling in appearance. This can be related back to the fact that methanol is more electrically conductive than ethanol. However, zinc or zinc-plated components would be much better than aluminium for use with the oxygenates. Copper can be used in the carburettor but care must be taken since this metal can yield large amounts of oxide in the presence of methanol with consequent danger to needle valves and generally inefficient fuel metering.

Conclusions

Our results point the way to material selection for the next generation of carburettors. However, existing materials were not shown to be in imminent danger of corrosive collapse after use of oxygenates. These corrosion studies were carried out in parallel with wide ranging studies of oxygenate fuel performance in a Fiat 127 903cc engine. Visual inspection of the carburettor on this engine after 3-4 years of use with oxygenates and with oxygenate/gasoline blends showing that some pitting of the carburettor had occurred. It is difficult to predict the useful life of carburettor components under these circumstances but this could reasonably be estimated to be several years. It must also be noted that carburettors have until now been largely designed for use with hydrocarbon fuels. As oxygenates begin to feature more prominently as potential alternatives, carburettor design will almost certainly change to use more resistant materials.

Furthermore many of the existing carburettor materials might be retained if some form of inexpensive protective coating were used. These may include polymeric or metallic coating on entire surfaces such as the carburettor body or inlet ducts etc., or on specific vulnerable areas such as the point of a needle valve.

In many countries of the world a finite percentage of alcohol is already used as an extender and to enhance resources of motor fuels. Research studies of this type provide clear indications of where engine designers must seek alternative construction materials for some components.

References

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Figure 1. Main Types of Growth Laws (2.)

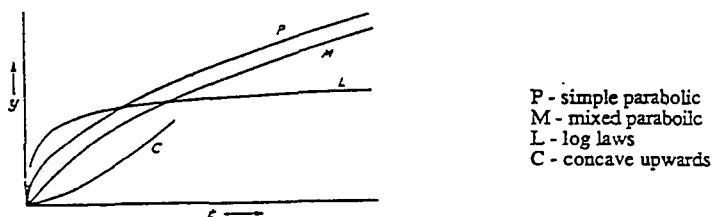


FIG. 2 THE OXIDATION AND CORROSION OF ZINC IN METHANOL/GASOLINE BLENDS AT 50 C

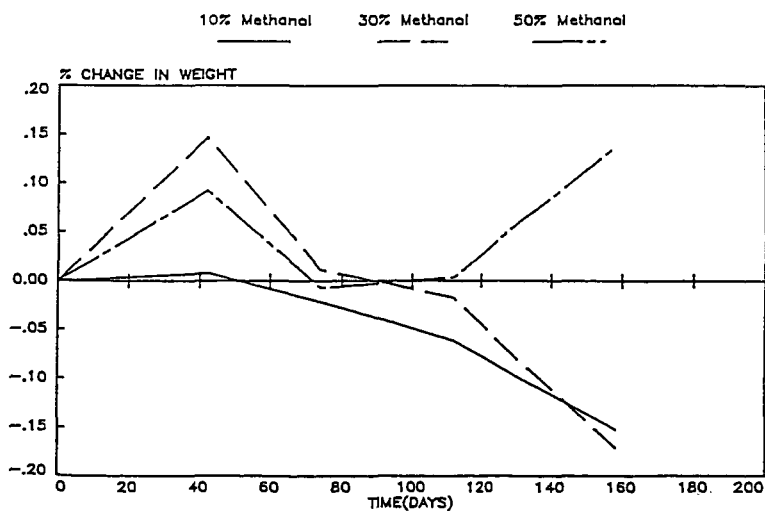


FIG. 3. EFFECT OF TEMPERATURE AND FORMIC ACID ON
OXIDATION AND CORROSION OF ALUMINIUM

